



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: B32B 27/40, B32B 27/08, B41M 1/26	A1	(11) International Publication Number: WO 00/00352 (43) International Publication Date: 06 January 2000 (06.01.2000)
(21) International Application Number: PCT/GB98/02096 (22) International Filing Date: 16 July 1998 (16.07.1998) (30) Priority Data: 09/107,302 30 June 1998 (30.06.1998) US (60) Parent Application or Grant HUNT GRAPHICS EUROPE LTD. [/]; (). COOK, Colin, John [/]; (). COOK, Colin, John [/]; (). MARLOW, Nicholas, Simon ; ().		Published
(54) Title: PRINTABLE LAMINATE (54) Titre: STRATIFIE IMPRIMABLE (57) Abstract <p>The present invention relates to a printable laminate and method for transferring a printed image onto a substrate. The printable laminate includes a transparent or clear film carrier with an image recording layer of a mixture of a heat activated adhesive, such as a polyurethane, and ink absorbing material, such as an ink absorbent modified cellulose material. After transfer of the image to the substrate the carrier layer remains attached to the image recording layer aiding in the appearance and protection of the image.</p> (57) Abrégé <p>Cette invention se rapporte à un stratifié imprimable et à un procédé servant à transférer une image imprimée sur un substrat. Ce stratifié imprimable comporte un support en film transparent avec une couche d'enregistrement d'image constituée d'un mélange d'un adhésif thermoactivé tel que du polyuréthane, et d'un matériau absorbant l'encre, tel qu'une matière cellulosique modifiée absorbant l'encre. Après le transfert de l'image sur le substrat, la couche du support reste fixée à la couche d'enregistrement de l'image, ce qui contribue à améliorer l'aspect de l'image et à la protéger.</p>		

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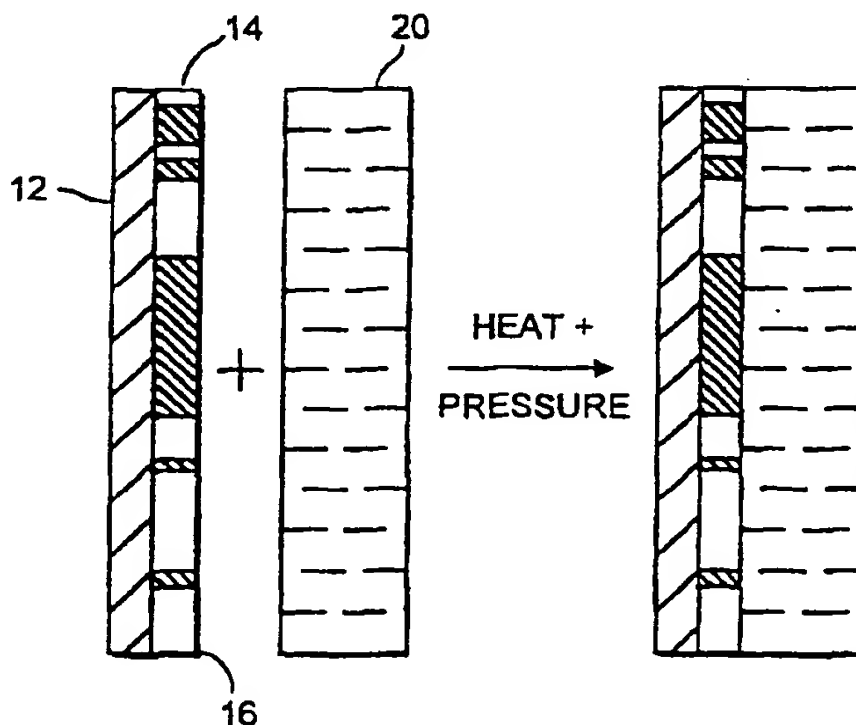
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(21) International Application Number: PCT/GB98/02096 (22) International Filing Date: 16 July 1998 (16.07.98) (30) Priority Data: 09/107,302 30 June 1998 (30.06.98) US (71) Applicant (for all designated States except US): HUNT GRAPHICS EUROPE LTD. [GB/GB]; Chester Hall Lane, Basildon, Essex SS14 3BG (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): COOK, Colin, John [GB/GB]; 2 Lombardy Close, Pitsea, Basildon, Essex SS13 2RE (GB). (74) Agent: MARLOW, Nicholas, Simon; Reddie & Grose, 16 Theobalds Road, London WC1X 8PL (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: PRINTABLE LAMINATE

(57) Abstract

The present invention relates to a printable laminate and method for transferring a printed image onto a substrate. The printable laminate includes a transparent or clear film carrier with an image recording layer of a mixture of a heat activated adhesive, such as a polyurethane, and ink absorbing material, such as an ink absorbent modified cellulose material. After transfer of the image to the substrate the carrier layer remains attached to the image recording layer aiding in the appearance and protection of the image.



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Description

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PRINTABLE LAMINATE

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The present invention relates to the transfer of a printed image onto a target substrate, especially foam board or rigid PVC.

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5 A wide variety of techniques have recently been developed for digitally capturing an image in the form of a computer-readable file, editing the image with the computer, printing the edited image onto a recording medium, and then transferring the image from the recording medium to a target substrate. Such target substrate can be fabric, ceramic, or, in the case of greatest significance for the present invention, foam board or rigid PVC, as used for example, in the commercial graphics industry.

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Through further investigation of the efficacy of the various reagents mentioned in said International Application, it has been discovered that the combination of polyurethane adhesive and a soluble ink absorber in

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the wet formulation produces a noticeable change in the nature of the porosity of the dry, image-recording layer, and an exceptionally strong bonding not only between the recording layer and the target substrate, but also between the recording layer and the carrier.

The carrier is preferably in the form of a substantially transparent or clear film, with the recording layer carried thereon presenting a relatively homogeneous, filmic surface for receiving and absorbing the ink. This combination of carrier and recording layer can be considered a printable laminate, i.e., it can record an image created through common printing techniques, most suitably, ink-jet printing techniques, and it can then be permanently laminated in its entirety to a target substrate, utilizing a conventional range of laminating temperatures and pressures.

The carrier can be any transparent or clear material compatible with the materials of the recording layer and capable of withstanding the heat and pressure of the laminating process. The carrier must also adhere to the recording layer sufficiently well after lamination and provide adequate protection of the underlying image printed on the image recording layer. The materials suitable for use as the carrier include cast films such as those made from polyolefin, polyesters, nylon and polyvinyl chloride. Polyesters, polyolefins and polyvinyl chloride appear to have particular suitability as the carrier of the present invention.

The polyurethane and the ink absorber together comprise at least 90%, and preferably at least 95% of the dry weight of the recording layer with optionally one or more defoamers and wetting agents comprising at least some of the balance of the dry weight of the recording layer. The polyurethane typically comprises

5 at least 50% of the dry weight of the image recording layer, while the ink absorber comprises at least 30% of the dry weight of the recording layer.

10 The polyurethane for use in the invention is preferably an aqueous dispersion of polyurethane which, if dried, forms a film of material. Upon application of heat and optionally pressure, the polyurethane is able to form an adhesive bond to other surfaces. In addition, it is preferable for the purposes of this invention that the polyurethane in combination with the ink absorptive material does not form a matrix of particles. To this end it is most preferable that the polyurethane have a small strand-like conformation so that in combination, the polyurethane and ink absorber form a more homogenous mixture. A polyurethane strand size of around 0.2 microns appears to be highly suitable for making the film. The polyurethane dispersion sold under the trademark Luphen D DS 3507 and available from BASF Corp, Mount Olive, New Jersey is particularly suitable for use in this invention.

20 The ink absorber is preferably a modified cellulose material and more preferably is a thermoplastic modified cellulose material. Suitable ink absorbers include hydroxypropyl cellulose and cellulose gum. Utilizing a thermoplastic ink absorber material permits plasticizing (softening) of the absorber at the temperatures in the range in which the laminate is bonded to a substrate. It is believed that this assists the laminate in making better contact with and improves adhesion to the substrate.

30 One particular thermoplastic modified cellulose of utility in the invention is Klucel E modified cellulose powder, commercially available from Hercules, Wilmington, Delaware. Other suitable materials include Blanose cellulose gum (sodium carboxymethylcellulose)

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and Glascol DP6 (cationically charged water-soluble polymer). Typically, the ink absorber is a very fine particulate material which, when dissolved in water, is of a molecular size. The dry particle size for a material such as Klucel E is estimated to be in the range of 0.003-0.2 microns. It will be appreciated that these ink absorptive materials may work with a variety of inks, dyes and image forming (printing) processes. However, it has been found that these ink absorber materials work particularly well with the ink-jet printing process and ink-jet inks, especially those inks which are dye-based and which are in water-based or water and glycol-based systems.

The defoaming and wetting agents for use in the invention are surfactants which may be anionic, cationic or nonionic in nature. The surfactants are intended to serve one or more functions in the invention, including: reducing bubble or foam formation in the image recording layer; promoting adequate wetting out and uniform formation of the recording layer on the carrier and promoting ink or dye absorption and diffusion in the carrier layer. Non-limiting examples of suitable surfactants for use in the invention include the nonionic surfactant sold under the trademark Pluronic PE6100, and the anionic surfactant sold under the trademark Lumiten I-AFK, both of which are commercially available from BASF Corp., Mount Olive, New Jersey.

The recording layer is preferably formed by mixing in a water-based system: (a) an aqueous polyurethane dispersion; with (b) a water-soluble, powdered ink absorber; and (c) one or more defoamer/wetting agents. This mixture is coated onto the carrier film, and dried below the minimum film forming temperature (MFFT) of the polyurethane dispersion.

Accordingly, the invention in one aspect is a

printable laminate comprising a substantially transparent film carrier having opposite first and second sides; a thermoplastic recording layer having an inner surface directly supported by one of said sides of the carrier and an exposed outer surface for receiving printing ink; wherein said recording layer comprises a heat activatable polyurethane adhesive and ink absorber which together constitute at least 90% of the total weight of the recording layer.

In another aspect of the invention a printed laminate comprises a substantially transparent film carrier having opposite first and second sides; a substantially clear thermoplastic recording layer having an inner surface directly supported by one of said sides of the carrier and an exposed outer surface, said recording layer comprising a heat activatable adhesive and an ink absorber which together constitute at least 90% of the total weight of the recording layer; and an ink pattern printed on said recording layer and extending from the outer surface to the inner surface of the recording layer.

In another aspect of the invention a method of producing a substantially permanent image on a substantially flat target surface, comprises selecting a printable laminate consisting of a substantially transparent film carrier having opposite first and second sides, and a substantially homogeneous recording layer in which the two most significant constituents by weight per cent are heat-activatable adhesive and ink absorber, wherein said recording layer has an inner surface directly supported by the first side of the carrier, and an exposed outer surface; printing ink in a pattern onto the exposed surface of the recording layer, wherein said ink diffuses through the layer to the inner surface of the layer without substantial

alteration of said pattern; placing the outer surface of the printable laminate on said target surface; and applying heat and pressure to the second surface of the carrier, thereby permanently adhering the outer surface of the recording layer to the target surface and the carrier to the inner surface of the recording layer.

One embodiment of the invention will be described below with reference to the accompanying drawings, wherein

FIG.1 shows the printable laminate according to the invention, with an ink pattern printed thereon; and

FIG.2 shows schematically how the printed laminate is used to decorate a target substrate.

Figure 1 shows the printable laminate 10 according to the invention, consisting essentially of a substantially transparent carrier film 12 having first and second surfaces, and a recording layer 14 having an inner surface directly covering the first surface of the carrier film, and outer exposed surface. An image 16 has been printed on the exposed surface of layer 14, as by an ink-jet printer (not shown), resulting in a pattern of distinct ink deposits such as 18, which have diffused through the thickness of the layer 14 without substantial degradation.

As shown in Figure 2, the outer surface of the printed laminate 10 is placed on a target surface of, e.g., a foam board or rigid sheet of PVC 20, and permanently adhered thereto by the application of heat and pressure through the second surface of the carrier film 12. According to the invention, this heat and pressure also permanently adheres the first surface of the carrier film to the inner surface of the recording

layer. This provides a protective covering for the printed image, without significantly affecting the observed quality of the image.

It should be understood that the temperature and pressure conditions associated with the process shown in Figure 2, are within the range of convention, as is described in the material incorporated herein by reference. It should also be understood that the term "permanent" with reference to adhesion, means the useful life of the decorated board or sheet under normal care and handling.

The carrier is preferably a 50-micron clear polyester, polyvinyl chloride or polypropylene film, which requires no special surface treatment. In particular, no melt transfer or release layer is provided.

The recording layer 12 is constituted on a weight basis, as follows:

	<u>Material</u>	<u>Function</u>	<u>General Percent</u>	<u>Preferred Percent</u>
20	Polyurethane	Heat activated adhesive	50-70	60-65, esp. 61.50
35	Hydroxypropyl Cellulose	Thermoplastic ink absorber	30-50	30-35, esp. 34.65
25	Ethylene Oxide- Propylene Oxide Copolymer	Nonionic surfactant	0-5	1-2, esp. 1.73
40	Sulfated Fatty Acid	Anionic surfactant	0-5	2-3, esp. 2.12

The recording layer is initially formulated as a coatable mixture, wherein the coating for the especially preferred layer is constituted on a weight basis as follows:

	<u>Material</u>	<u>Form or Function</u>	<u>Percentage</u>
50	Luphen D DS 3507	Polyurethane dispersion in water	28.06

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	Klucel E	Water-soluble modified cellulose powder	7.11
5	Pluronic PE6100	Defoamer/wetting agent	0.36
	Lumiten I-AFK	Wetting agent	0.79
	Water	Diluent	63.68

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The resins in the foregoing formulation are preferably of an extremely fine size (in the range of about 0.003 - 0.2 microns), i.e., generally finer than the particle size range of 0.08-3 micron described in said International Application. As a result, upon drying of the coating at a temperature below the MFFT of the adhesive dispersion a filmic yet microporous recording layer is formed. It is believed that the adhesive and absorber mix substantially randomly at the molecular level, providing substantial homogeneity of the recording layer, rather than a porous matrix of distinct adhesive particulates bound together by the absorber. The clarity of the coating upon drying, may also be attributable to this intimate homogeneity.

This surprising result is believed to arise at least in part by the larger number of water molecules that form the polyurethane polymer, being replaced by molecules of the absorber material, as the coating is dried.

The advantages of laminates according to the invention include (1) sharper printing resolution on the recording layer, (2) clarity of the recording layer, and (3) the high adhesive strength of polyurethane for holding the recording layer to the target surface and the carrier to the recording layer. The drying temperature is held below the MFFT of the adhesive dispersion. For example, the MFFT of the polyurethane dispersion Luphen D DS 3507 is about 60°C and the heat activation temperature of the entire laminate is typically in the range of 75° to 125°C.

Claims

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C L A I M S :

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1. A printable laminate comprises :
a substantially transparent film carrier having opposite first and second sides;

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a thermoplastic recording layer having an inner surface directly supported by one of said sides of the carrier and an exposed outer surface for receiving printing ink;

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wherein the recording layer comprises a heat activatable polyurethane adhesive and an ink absorber which together constitute at least 90% of the total weight of the recording layer.

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2. A printable laminate according to claim 1, wherein the polyurethane weight is at least 50% of the total weight of the recording layer.

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3. A printable laminate according to claim 1 or 2, wherein the polyurethane weight is in the range of about 50-70 weight % of the total weight of the recording layer.

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4. A printable laminate according to any preceding claim wherein the ink absorber is at least 30% of the total weight of the recording layer.

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5. A printable laminate according to any preceding claim wherein the heat activatable polyurethane adhesive and ink absorber together constitute at least 95% of the total weight of the recording layer.

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6. A printable laminate according to any preceding claim wherein the ink absorber is a modified cellulose.

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7. A printable laminate according to any preceding claim wherein the ink absorber is one or more members selected from the group consisting of hydroxypropyl cellulose or sodium carboxymethyl cellulose.

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- 5 8. A printable laminate according to any preceding claim wherein the ink absorber is a cationically charged water-soluble polymer.
- 10 9. A printable laminate according to any preceding claim wherein the recording layer comprises:
- 5 polyurethane in the range of about 60-65 weight %;
hydroxypropyl cellulose in the range of about 30-35 weight %; and
up to about 5% surfactants.
- 15 10. A printable laminate according to any preceding claim, wherein the carrier is one of clear polyester or clear polypropylene film.
- 20 11. A printable laminate according to any preceding claim, wherein the recording layer is substantially clear.
- 25 12. A printed laminate comprising :
a substantially transparent film carrier having opposite first and second sides;
a substantially clear thermoplastic recording layer having an inner surface directly supported by one of said sides of the carrier and an exposed outer surface, said recording layer comprising a heat activatable adhesive and an ink absorber which together constitute at least 90% of the total weight of the recording layer; and
an ink pattern printed on said recording layer and extending from the outer surface to the inner surface of the recording layer.
- 30 13. A printed laminate according to claim 12, wherein the heat activatable adhesive is polyurethane having a strand size of about 0.2 microns and constituting at least 50% of the weight of the recording layer exclusive of ink.
- 35 14. A printed laminate according to claim 12 or 13 wherein the thermoplastic ink absorber is at least 30% of the total
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weight of the recording layer exclusive of ink.

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15. A printed laminate comprising :

a printable laminate according to any of claims 1 to 11; and

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an ink pattern printed on the recording layer and extending from the outer surface to the inner surface of the recording layer.

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16. A method of producing a substantially permanent image on a substantially flat target surface comprising the steps of :

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a) selecting a printable laminate consisting of a substantially transparent film carrier having opposite first and second sides, and a substantially homogeneous recording layer in which the two most significant constituents by weight % are heat-activatable adhesive and ink absorber, wherein said recording layer has an inner surface directly supported by the first side of the carrier, and an exposed outer surface;

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b) printing ink in a pattern onto the exposed surface of the recording layer, whereby said ink diffuses through the later to the inner surface of the layer without substantial alteration of said pattern;

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c) placing the outer surface of the printable laminate on said target surface; and

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d) applying heat and pressure to the second surface of the carrier, thereby

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permanently adhering the outer surface of the recording layer to the target surface and the carrier to the inner surface of the recording layer.

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17. A method according to claim 16, wherein the heat-activatable adhesive is polyurethane.

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18. A method according to claim 17 wherein before the step

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of printing, the recording layer is substantially clear.

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19. A method according to claim 17 or 18, wherein the target surface is one of foam board or rigid PVC.

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20. A printable laminate substantially as hereinbefore described.

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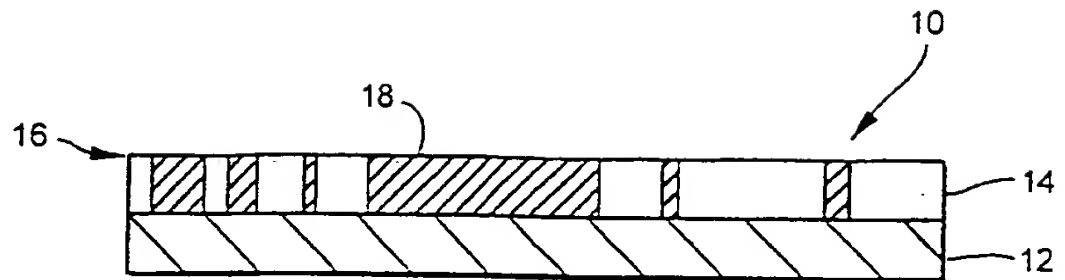


FIG. 1

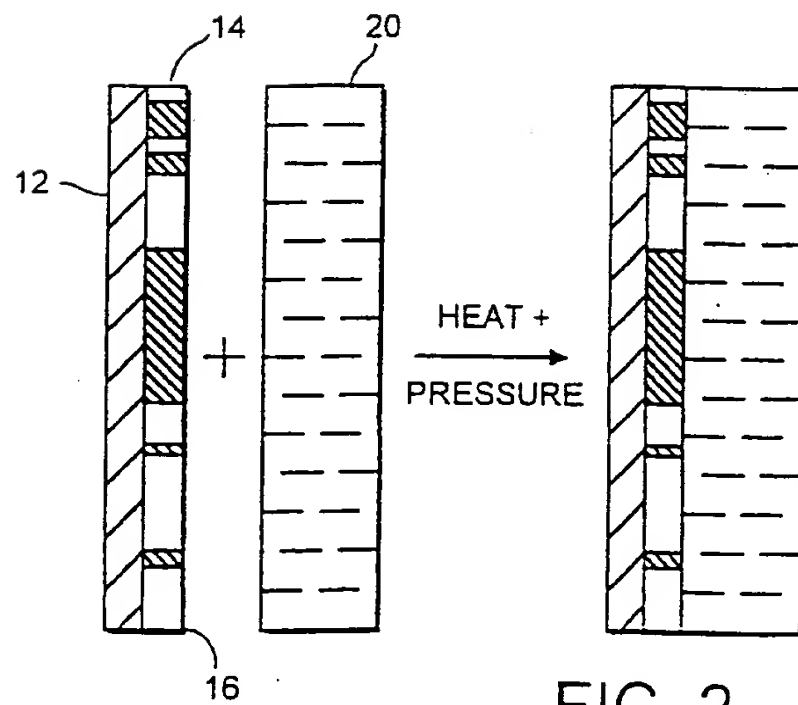


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 98/02096

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B32B27/40 B32B27/08 B41M1/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 06564 A (REXHAM GRAPHICS INC) 9 March 1995 see page 8, line 5 - line 33 see page 9, line 6 - line 11 ----	1-15
A	US 5 672 413 A (CAHILL DOUGLAS ALLAN ET AL) 30 September 1997 see column 3, line 23 - line 24 see column 3, line 65 - line 67 ----	1-15
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 008, 30 August 1996 & JP 08 099458 A (TEIKOKU INK SEIZO KK; SONY CORP), 16 April 1996 see abstract -----	1-15

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☒ Patent family members are listed in annex

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Date of the actual completion of the international search

11 March 1999

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24/03/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9506564 A	09-03-1995	US 5795425 A	18-08-1998
		US 5766398 A	16-06-1998
		AU 7674794 A	22-03-1995
		DE 716633 T	28-11-1996
		EP 0716633 A	19-06-1996
		JP 9503168 T	31-03-1997
		US 5837375 A	17-11-1998
US 5672413 A	30-09-1997	NONE	